

Highly sensitive XAS with Single X-Ray Pulses at 1 kHz

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INTRODUCTION

We are currently developing a scheme to exploit pulsed x-radiation for structural dynamics studies at beamline 5.3.1 via time-resolved X-ray absorption spectroscopy (XAS). While XANES is complicated to interpret from a structural point of view, it contains rather simple phenomena like the chemical shift, which describes the oxidation state of the atom. On the other hand, EXAFS delivers a detailed picture of the local environment [1], and interatomic separations can nowadays be determined with an accuracy down to 100 fm [2]. In addition, EXAFS requires no periodic structures (as required in x-ray diffraction), and can be readily applied to disordered systems, e.g., liquids.

Laser-pump SR-probe experiments depend on the available number of x-ray photons per single pulse at the repetition rate of the exciting laser, which is typically 1 kHz for commercial amplified fs-lasers. Therefore, such experiments can use only about 10^{-5} - 10^{-6} of the available photon flux at a synchrotron with its much higher pulse repetition rate of 100 - 500 MHz. We have performed calculations of the expected pump-probe signal for a given condensed phase chemical system [3,4], which also underline the general utility of time-resolved XAS in condensed phase dynamics research.

EXPERIMENTAL APPROACH

X-radiation from the ALS camshaft pulse (detected with an APD behind the sample) is singled out with a gated integrator (opening window ca. 20 ns). In order to record high-quality spectra in a pump-probe configuration we have employed the following scheme: The gated integrator is triggered at twice the laser repetition rate, so that every second x-ray pulse corresponds to the static (= unexcited) sample, while the other x-ray pulses monitor the transmission following photoexcitation at an adjustable time delay. Therefore, the gated integrator delivers an output of alternatively laser-pumped and unpumped intensities, which are then read into the computer and appropriately sorted. With this scheme we can record high-quality EXAFS spectra of the photoinduced changes. Indeed, a careful analysis of the measured noise shows that we have nearly achieved the shot noise limit in this configuration. The measured noise is considerably reduced over other methods, which include additional systematic noise sources. The step-scanning monochromator induces vibrations, which result in a rather constant noise source on the transmitted intensity. This is considerably reduced, when no optics move, and the decreasing storage ring current is observed by a corresponding broadening of the pulse height distribution. In addition, using our latest development by measuring the difference spectra *during* a monochromator scan reduces the noise even more. After correcting the statistically derived effective flux for the limited x-ray absorption in the 30 μm thick APD, our measurements are very close to the specified flux of this beamline [5].

RESULTS AND DISCUSSION

With our new difference-signal detection scheme we make best use of the x-ray source, since the recorded noise on these spectra correspond nearly entirely to the expected shot noise limit. But we can also record high-quality EXAFS without employing the difference measurement technique. Figure 1 illustrates this for the case of aqueous iodide. The energy spectrum has already been transformed into k -space (Fig. 1a), but the original data has not been treated (e.g., smoothed or Fourier-filtered). This spectrum represents a single scan accumulating 2500 single x-ray pulses per data point. The fit (and its Fourier transform, Fig. 1b) delivers a nice agreement with the literature, and the accuracy for determining the nearest neighbor shell of oxygen atoms is better than 10 pm [4].

Fig. 1 also illustrates the potential for measuring the nearest-neighbor distance in photogenerated iodine radicals. The I-O distance should change considerably upon photodetachment. Values for iodine are currently unknown, but in a theoretical study of aqueous Br radicals the predicted Br-O distance changed from 335 pm for the ion to ca. 280 pm for the neutral radical [6]. Assuming a similar reduction in the iodine-oxygen distances would result in a pronounced change in the EXAFS signal, as shown in the dashed curves in Fig. 1.

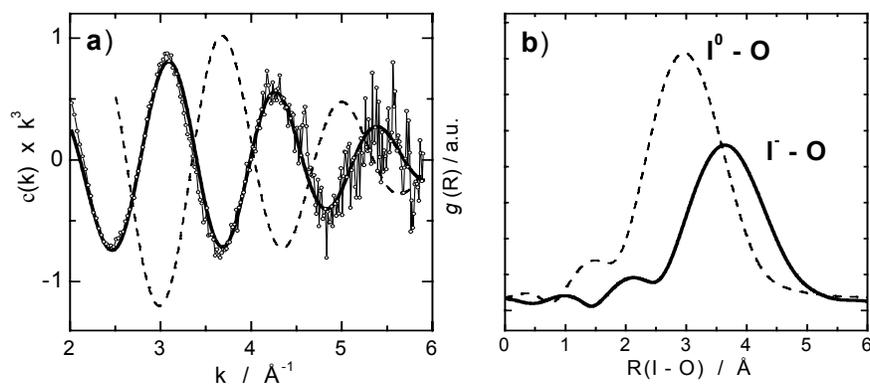
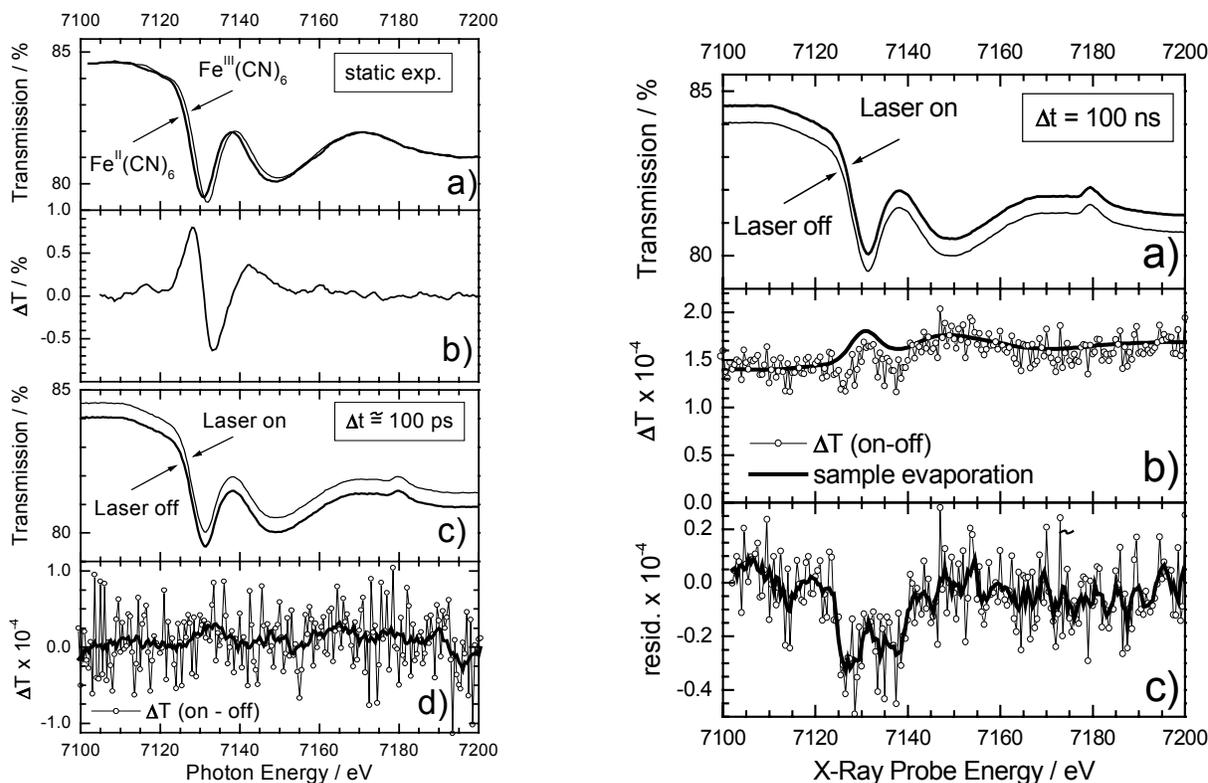


Figure 1. Static EXAFS above the L_3 edge of iodine of aqueous iodide (NaI concentration: 0.7 mol/l, thickness: 0.1 mm). Original data (open circles), and their fit (solid line) is shown in a), and the Fourier transform showing the nearest neighbor I-O distance in b) (solid line). For comparison, a simulation of the expected EXAFS of atomic iodine is shown (dashed curve in a) together with its Fourier transform (dashed curve in b).

Exploiting our difference measurement technique we have attempted to measure the photo-induced chemical shift due to UV photoionization of the central Fe atom in aqueous $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ with a synchronized fs laser. The chemical shift of ca. 1 eV around the Fe K edge was observed in static samples containing either $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ or $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ (concentration 0.2 mol/l, sample thickness 0.1 mm), as illustrated in Fig. 2 a) and b). Then we excited a liquid jet with the reactant species $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ only with 100 μJ of 266 nm light, and recorded the transient changes. Due to the low excitation yield of below 0.4 % we could not observe the chemical shift on the 100 ps time scale (Fig. 2 c) and d). However, with improved statistics exploiting the first 100 ns of the multibunch train following photoexcitation we did observe a photoinduced change in the XAS. In Fig. 3 a) the average of 20 spectra are shown for each the unpumped and the pumped sample (offset for clarity). Fig. 3 b) shows the difference signal of Fig. 3 a) together with a simulation assuming laser-induced evaporation of ca. 100 nm of the 0.1 mm thick sample. While this nicely reproduces the majority of the measured difference spectrum, we still observe some discrepancy around the $1s \rightarrow 4p$ pre edge feature, as shown in the residual spectrum in Fig. 3 c). The double minimum shape of decreased transmission (clearly visible in the smoothed spectrum) indicates a

broadening of this feature, which has been observed in temperature-dependent XANES studies. The elevated temperature of the laser-heated sample could account for this observation. While our current sensitivity does not allow to unambiguously observe the chemical shift for less than 0.4 % excited species, current improvements on the laser excitation process will permit us to boost the product yield into the 1-5 % range.



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